SEMI-INSULATING GROUP III METAL NITRIDE AND METHOD OF MANUFACTURE

CROSS-REFERENCE TO RELATED APPLICATION

This patent application claims priority from U.S. patent application Ser. No. 61/313,112, filed Mar. 11, 2010, and entitled "Improved Semi-Insulating Group III Metal Nitride and Method of Making."

BACKGROUND OF THE INVENTION

The present invention generally relates to processing of materials for growth of crystals. More particularly, the present invention provides a semi-insulating gallium-containing nitride crystal synthesized by an ammonobasic or ammonoacidic technique. The present invention provides methods suitable for synthesis of polycrystalline nitride materials, as well as other crystals and materials. Such crystals and materials include, but are not limited to, GaN, AN, InN, InGaN, AlGaN, and AlInGaN, and for manufacture of bulk or patterned substrates. Such bulk or patterned substrates can be used for a variety of applications including optoelectronic devices, lasers, light emitting diodes, solar cells, photoelectrochemical water splitting and hydrogen generation, photodetectors, integrated circuits, and transistors.

Gallium nitride containing crystalline materials serve as substrates for manufacture of conventional optoelectronic devices, such as blue light emitting diodes and lasers. Such optoelectronic devices have been commonly manufactured on sapphire or silicon carbide substrates that differ in composition from the deposited nitride layers. In the conventional Metal-Organic Chemical Vapor Deposition (MOCVD) method, deposition of GaN is performed from ammonia and organometallic compounds in the gas phase. Although successful, conventional growth rates achieved make it difficult to provide a bulk layer of GaN material. Additionally, dislocation densities are also high and lead to poorer optoelectronic device performance.

Quality substrates comprising bulk gallium nitride are available commercially, however, in most cases, these substrates are electrically conductive. In some cases, a substrate that is electrically insulating or semi-insulating is desirable. In addition, bulk gallium nitride substrates are generally expensive, and substrate diameters of 2 inches and larger are only available with a c-plane orientation.

Several authors have disclosed the addition of transition metal deep acceptor dopants, e.g., Mn, Fe, Co, Ni, Cu, etc., to compensate donor species in the gallium nitride, and impart semi-insulating character to the gallium nitride. For example, Monemar and Lagerstedt [J. Appl. Phys. 50, 6480 (1979)] added Fe or Cr to GaN grown by hydride vapor phase epitaxy (HVPE) and obtained highly resistive crystals. Heikman et al. [Appl. Phys. Lett. 81, 439 (2002)] introduced Fe into GaN films grown by metalorganic chemical vapor deposition (MOCVD) and similarly obtained semi-insulating character. Generally, these authors were not able to obtain high quality, free standing bulk GaN wafers.

U.S. Pat. No. 6,273,948, issued to Porowski et al., describes a method of fabricating highly resistive GaN bulk crystals by crystallization from a solution of atomic nitrogen in a molten mixture of gallium and Group II metal such as beryllium or calcium, under a high pressure of about 0.5-2.0 GPa and a high temperature of 1300-1700 degrees Celsius. A resistivity of 10^4 to 10^8 ohm-centimeter (ohm-cm) was achieved. The crystal obtained from the process was about 1 cm in size, whereas most commercial electronic applications require a substrate size of at least about 2 inches (>5 cm) diameter.

U.S. Pat. No. 7,170,095, issued to Vaudo et al., describes an improved HVPE method for doping free-standing GaN crystals with relatively high crystalline quality. The HVPE technique, however, generally produces bulk GaN crystals of relatively high cost. U.S. Pat. No. 7,078,731, issued to D'Evelyn et al., teaches an ammonothermal method for synthesizing semi-insulating GaN crystals, for example, by doping with Fe or Co. The Fe-doped and Co-doped GaN crystals, however, are reddish/amber or black in color, respectively, rather than transparent and colorless.

What is needed is a method for low-cost manufacturing of semi-insulating nitride materials that are transparent, colorless, and of high crystallographic quality.

DETAILED DESCRIPTION OF THE INVENTION

Approximating language, as used herein throughout the specification and claims, may be applied to modify any quantitative representation that could permissibly vary without resulting in a change in the basic function to which it may be related. Accordingly, a value modified by a term such as "about" is not limited to the precise value specified. In at least one instance, the variance indicated by the term "about" may be determined with reference to the precision of the measuring instrumentation. Similarly, "free" may be combined with a term; and, may include an insubstantial number, or a trace amount, while still being considered free of the modified term unless explicitly stated otherwise.

The metal of a metal nitride may include a group III metal. Suitable metals may include aluminum, gallium, and indium. The "one or more" refers to combination of metals in the metal nitride, and may include compositions such as aluminum gallium nitride (AlGaN), and the like. As used herein, the term "gallium nitride" will be used as an illustrative example of a metal nitride, but it is understood that other group III metal nitrides are also possible.

A metal nitride composition may contain impurities. As used herein, the term "impurity" refers to a chemical species that is distinct from the group III metal nitride that constitutes the majority composition of the single-crystal or polycrystalline metal nitride. Several classes of impurities may be distinguished, with respect to chemistry, atomic structure, intent, and effect. Impurities will generally comprise elements distinct from nitrogen, aluminum, gallium, and indium, including oxygen, carbon, halogens, hydrogen, alkali metals, alkaline earth metals, transition metals, and main block elements. The impurity may be present in a number of forms, with different atomic structure. In some cases, the impurity is present as an isolated atom or ion within the crystalline lattice of the group III metal nitride, for example, as a substitutional or interstitial impurity. In other cases, the impurity is present in a distinct phase, for example, as an inclusion within an individual group III metal nitride grain or within a grain boundary of the group III metal nitride. The impurity may be deliberately added, to enhance the properties of the group III metal nitride in some way, or may be unintentional. Finally, the impurity may or may not have a significant effect on the electrical, crystallographic, chemical, or mechanical properties of the group III metal nitride.

As used herein, and as is commonly used in the art, the term "dopant" refers to an impurity that is atomically dispersed within the group III metal nitride, for example, as a substitutional or interstitial impurity, and which is typically added intentionally. With regard to dopants and dopant precursors